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Dissolved Oxygen and pH Microelectrode Measurements at Water-Immersed Metal Surfaces*

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ABSTRACT

Dissolved oxygen (DO) and pH were measured at metal artificial seawater interfaces using microelectrodes in biotic and abiotic systems. Measurements in a closed system proved that presence of electrochemical and/or biological reaction products substantially influence the conditions at the metal surface. For long-term studies, only open (e.g., continuous flow) reactors should be used. An open channel flow reactor suitable both for microbiological and electrochemical measurements has been constructed and successfully tested.

INTRODUCTION

Investigation of microbial corrosion requires incorporation of both electrochemical and microbiological methods. Simple insertion of microorganisms into an electrochemical reactor may not yield useful or relevant information. Inserting corrosion coupons into a microbiological reactor may be similarly useless. Investigation of microbial corrosion requires integration of methods from both disciplines modified for specific measurements suitable for relevant experimental reactors.

Microbial colonization of a metal surface immersed in water changes the properties of the metal-water interface and influences the corrosion rate because of microbial metabolic activity.[1] The difference between corrosion rates in the absence and in the presence of microorganisms is called microbial corrosion. The microbial corrosion rate is a function of microbial activity at the metal surface. The kind and intensity of microbially induced changes at the metal surface depends on many factors, and hence, generalization of mechanisms for microbial corrosion is difficult. Microbial corrosion rate depends on the kind of microorganisms that colonize the metal surface, the electron donor and the electron acceptor in the microbial respiration chain, rate of microbial metabolic activity, physical and chemical properties of the bulk water, hydrodynamic flow regime at the metal surface, metal composition, physical and chemical properties of metal surface, corrosion inhibi-

tion program, and many other factors.

To understand mechanism of microbially induced corrosion it is imperative to describe exactly the conditions at the metal-water interface in terms of chemical composition. Thus far there are many theoretical speculations regarding these conditions. Theoretical calculations must be, however, verified by direct measurements. The authors of this paper believe that tools for such verification already exist—microelectrodes. Microelectrode technology for analytical purposes has made considerable progress. Microelectrodes for measurement of many inorganic ion activities in microenvironments have been constructed and successfully tested. Microelectrodes have found application mainly in the fields of physiology and medicine, but the same or a similar construction can be applied to describe conditions at the metal water interface. This paper describes the application of dissolved oxygen (DO) and pH microelectrodes for measurements at metal surfaces immersed in water. DO and pH are important factors for chemical description of the metal-water interface. Oxygen is the preferred electron acceptor for microbial respiration. Under aerobic conditions oxygen concentration decreases as the microbially colonized metal surface is approached. Areas of oxygen depletion on metal surface are anodic relative to surrounding areas. Reduction in oxygen concentration also creates conditions conducive for sulfate-reducing bacteria, even if the bulk medium has measurable DO concentration.[2] Microbial activity may also change the metal surface pH. High metal surface pH promotes formation of calcareous deposits, while low pH causes dissolution of deposits and exposure of the metal surface.[3] Little, et al.[4] suggest that pH at the microbially colonized metal surface can, in some cases, be as low as 0.6.

The performance of DO and pH electrodes were tested in a system that allowed comparison of measured and theoretical results. Cathodic polarization was chosen as a suitable system. During cathodic polarization, DO is reduced at the metal surface and a stoichiometrically predictable amount of hydroxyl ion is released. Thus, an increase in applied cathodic potential would cause DO concentration at the metal surface to decrease and pH to increase. This test, conducted under abiotic conditions, was undertaken to verify the applicability of the microelectrodes for description of conditions at the metal surface. Positive evaluation of microelectrode performance in an abiotic system (measured response corresponding to theoretical prediction) can justify their application in a biotic system where results are hard to predict.
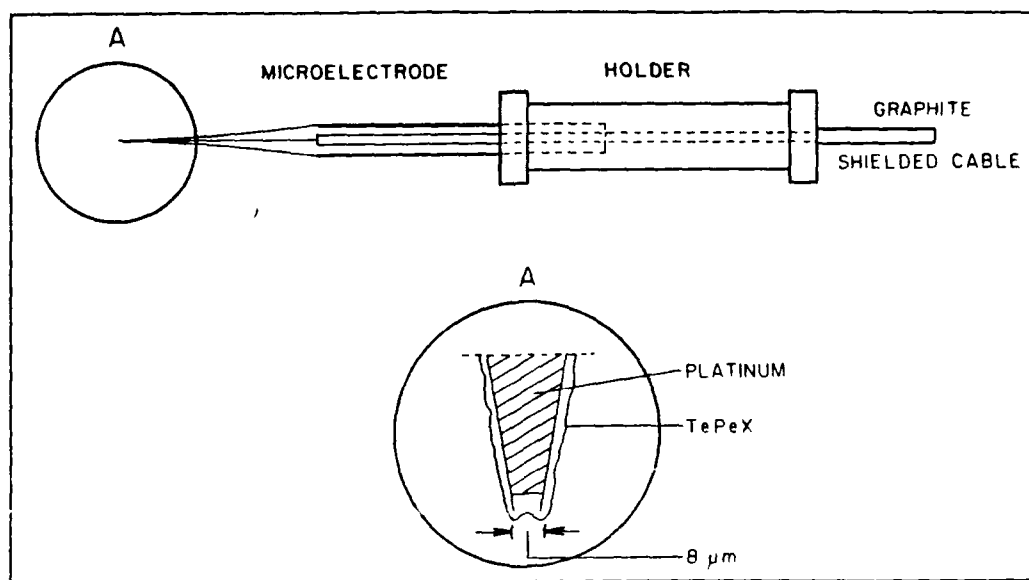
FIGURE 1. *DO microelectrode*

EXPERIMENTAL PROCEDURE

Dissolved Oxygen Electrode

The DO electrode. designed by Clark. et al .[5] was reduced to microelectrode size using a procedure described by Revsbech and Jorgensen.[6] The electrode was made of a 0.1-mm. high-purity (99.99%) platinum wire etched electrochemically with one end in KCN to a tip diameter of ~2 μm. The wire was rinsed with concentrated HCl and ethanol and covered with soda-lime glass. The tip of the platinum wire was exposed by grinding on a rotating wheel covered with diamond paste. The exposed platinum tip was subsequently etched in KCN to yield a recess of ~2 μm. The operation was performed with a microscope with a mounted TV camera and was observed on a video screen. The tip of the electrode was covered with a polymer (TePeX [ ]). serving as the oxygen-permeable membrane. The electrode was calibrated in 3.5% Instant Ocean[+] solution by aeration and subsequent purging with pure nitrogen. The current in the measuring circuit was measured with a picoammeter with output to a linear recorder. a sketch of a DO electrode is presented in Figure 1.

pH Electrode

The pH microelectrode was of a recessed type. The construction was a modification of that described by Thomas.[7] A micropipette made of lead glass (Corning[+] 0120) served as insulation. pH-sensitive glass (Corning 0150) was used as a membrane. The capillary made of pH-sensitive glass. sealed on one end. was inserted into the insulating lead glass pipette almost to the end. Application of pressure to the pH-sensitive glass capillary, along with careful heating of the sealed end with a heating loop. expanded the pH-sensitive glass inside the insulating glass. thereby providing a fused seal between the two glasses (Figure 2). All manipulations were performed using a light microscope. The electrodes were subsequently immersed in distilled water and were boiled gently for ~2 h to hydrate the pH-sensitive glass. Then. the distilled water in the microelectrodes was replaced with

FIGURE 2. *Microphotograph of a pH microelectrode*

0.1 M NaCl buffered to pH 6 with 0.1 M citrate buffer. The silver silver chloride (Ag/AgCl) wire was prepared by coating a silver wire (cleaned with nitric acid) with silver chloride by making it the anode in dilute hydrochloric acid. The wire was sealed inside the electrode shaft with silicone rubber. The recessed construction permits the electrode to touch a metal surface without breaking the pH-sensitive membrane. The difference in potential between the measurement and reference Ag/AgCl electrode was measured using an electrometer connected with an amplifier of 10^{12} ohms impedance. The electrode was calibrated using standard pH buffer solutions.

Electrodes for DO and pH were used in the following two reactors:

1. A closed. abiotic reactor for describing conditions at a cathodically polarized stainless steel (SS) coupon: and
2. An open channel reactor for measuring the DO profile in an artificial biofilm attached to SS corrosion coupons.

Artificial seawater (3.5% Instant Ocean) and 3.5% sodium chloride (NaCl) were used as the medium. Chemical composition of the Instant Ocean is presented in Table 1.

TABLE 1
*Ionic Composition of
3.5% Instant Ocean*

Ion		ppm
Chloride	[Cl⁻]	18.785
Sodium	[Na⁺]	10.424
Sulfate	[SO₄²⁻]	2577
Magnesium	[Mg²⁺]	1265
Calcium	[Ca²⁺]	396
Potassium	[K⁺]	371
Bicarbonate	[HCO₃⁻]	145
Borate	[BO₃³⁻]	28
Phosphate	[PO₄³⁻]	1.4
Solids Total		33.997.4

Closed Abiotic Reactor

Measurements in an abiotic, closed reactor were conducted to evaluate the electrode performance under well-defined conditions at the metal surface. The influence of cathodic polarization on interfacial DO concentration and pH was measured. Measurements were conducted in a 1-L volume PARC[2] flask equipped with two graphite counter electrodes, a SCE, and an Allegheny Ludlum[3] 6X (SS) working electrode (Figure 3). Cathodic polarization potential voltages were determined and maintained constant using a PARC 273 potentiostat-galvanostat. Applied potential was varied from 0 to −1.0 V(SCE) in 0.1-V intervals. Circular AL6X electrodes with a surface area of 1 cm² were cut from a 0.65-mm metal sheet. The working electrode was rinsed with acetone prior to mounting in the PARC flat electrode holder. DO and pH at the cathodically polarized metal surfaces were measured using microelectrodes positioned at the surface of the working electrode using a micromanipulator. Measurements of DO and pH were made against a standard Ag/AgCl electrode. During the measurements the reactor liquid was purged with air. Measurements were conducted in 3.5% artificial seawater (Instant Ocean) and 3.5% sodium chloride.

Open Biotic Reactor

Measurements in the presence of microorganisms were conducted in an open channel flow reactor with dimensions 1.00 x 0.15 m x 0.30 m (Figure 4). Twenty-four corrosion coupons made of AISI[4] 304 SS (1.59-cm inside diameter) were fixed in the reactor using sample holders and were connected to potentiostat. Corrosion coupons were prepared by polishing with 600-grit powder, degreasing with 100% ethanol, and rinsing with acetone. Twelve coupons were maintained as sterile control, twelve additional coupons were inoculated with mixed culture of microorganisms. A drop of activated sludge was placed on the coupon surface and covered with 0.5% agar. Subsequently, the agar-microbe mix was covered with 2% agar. The 2% agar prevented penetration of microorganisms from the bulk medium to the metal coupons. The pore size of 2% agar had been estimated to be 44 nm.[8] The present measurement (Figure 5) showed the pore size of 2% agar to be in the range of 10 to 60 nm. Consequently, bacteria from the liquid phase cannot penetrate through the 2% agar to the metal surface. On the other hand, the mixed culture originally immobilized remains trapped on the metal surface. The medium 3.5% artificial seawater (Instant Ocean) with 100-mgL⁻¹ yeast extract was supplied continuously and flowed over the reactor surface creating a suitable shear stress. The oxygen and nutrients were transported from the bulk medium by diffusion through the agar layer to the immobilized cells. The conditions at the corrosion coupons were evaluated by measuring the DO profile in the agar layer during cathodic polarization of the corrosion coupons. The first measurements were conducted just after inoculation, then repeated after 14, 38, and 52 h of reactor operation. After 38 h of reactor operation, glutaraldehyde was introduced for 14 h in the reactor influent at 500 mgL⁻¹.

The purpose of the glutaraldehyde treatment was to inactivate microorganisms at the metal surface and to compare conditions (microbial activity) with those at the beginning of reactor operation. After 52 h of operation (14 h of contact with glutaraldehyde) the DO profile and cathodic polarization measurements were repeated.
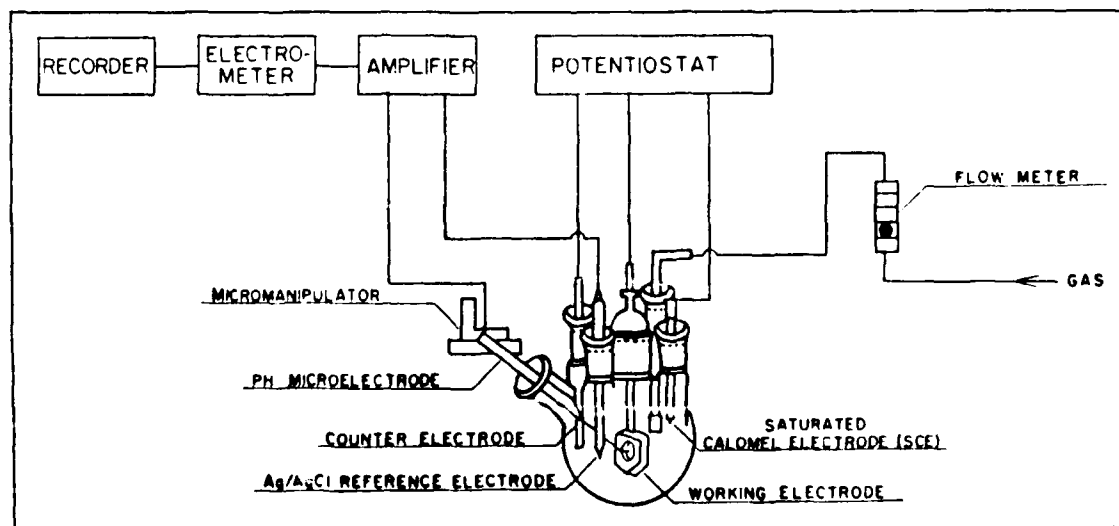

FIGURE 3. *Experimental apparatus for measurements of conditions at a cathodically polarized metal surface*
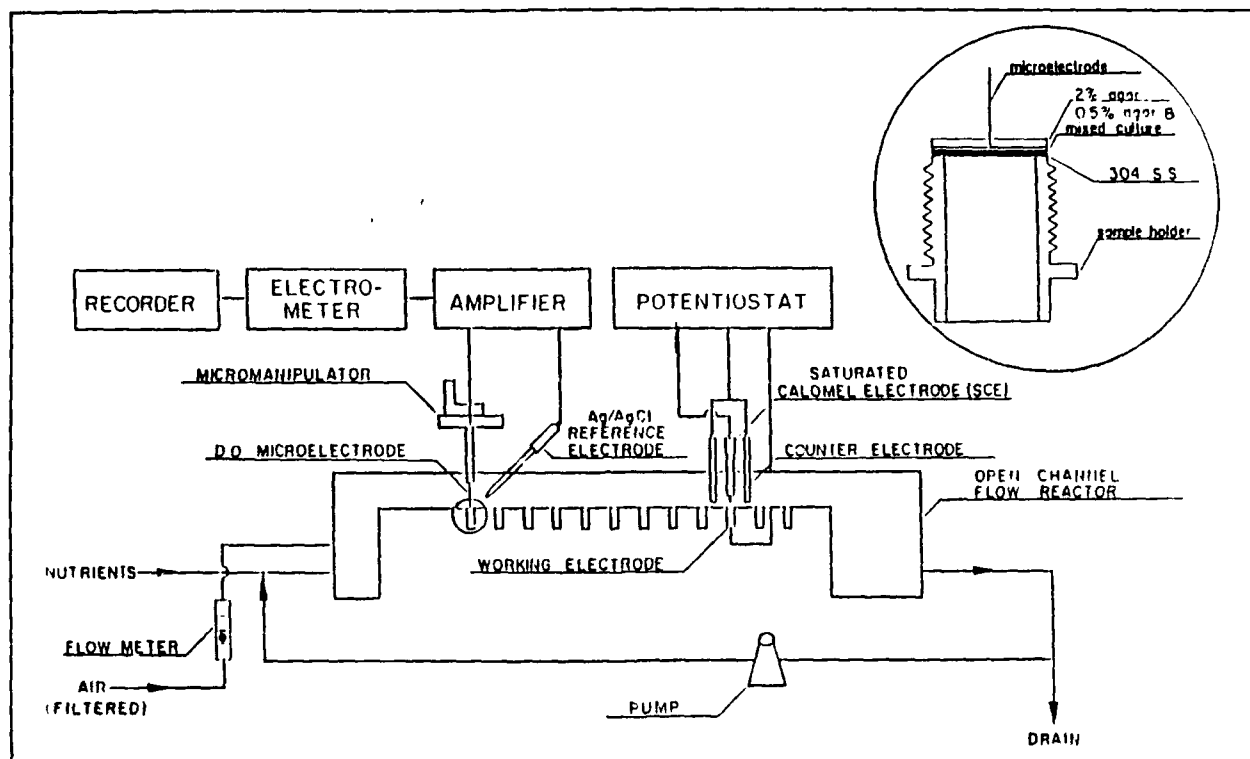
FIGURE 4. *The open channel flow reactor.*

FIGURE 5. *SEM micrograph of Acetobacter aceti in 2% agar matrix (the size of bar is equivalent to 200 nm).*

Agar Pore Size Measurement

The pore size of 2% agar was estimated by scanning electron microscopy (SEM). Agar discs colonized with *Acetobacter aceti* were fixed for 8 h in 2% glutaraldehyde diluted with filter sterilized artificial seawater. The agar discs were dehydrated in a graded series of ethanol (30 min in ethanol 30 to 100%). The agar discs were prepared for electron microscopy by critical point drying using a Balzers[5] CPD-020 critical point dryer. Samples were sputter-coated with Au-Pd alloy and were examined at 30,000X

(Figure 5) with a JEOL[6] 100 CX electron microscopy using an ASiD[7]-4D scanning attachment

EXPERIMENTAL RESULTS

Abiotic Experiment

Interfacial DO concentration at a cathodically polarized AL6X SS surface in aerated Instant Ocean measured (Figure 6). Results indicate that increasing applied potential to -0.3 V(SCE) did not change the DO at the metal surface. Further increase in applied potential resulted in rapid decrease in DO at the metal surface. Oxygen concentration reached zero when the applied potential reached -0.8 V(SCE). The curve reaches zero oxygen concentration asymptotically.

pH was measured at the cathodically polarized metal surface in 3.5% artificial seawater and 3.5% sodium chloride solution (Figure 7). pH reaches a plateau between -0.6 and -0.8 V(SCE) applied potential for artificial seawater and NaCl solution. The results correspond with DO consumption (Figure 6). Increase in applied potential over -0.8 V(SCE) in both cases resulted in further increased pH.

Biotic Experiment

Current density as a function of cathodic polarization was measured using corrosion coupons in the open channel flow reactor (Figure 8). Cathodic potential against a SCE was varied from corrosion potential E_{cor} to -0.6 V(SCE). The current density resulting from a specific imposed potential decreased considerably with run time. Glutaraldehyde treatment reversed this tendency
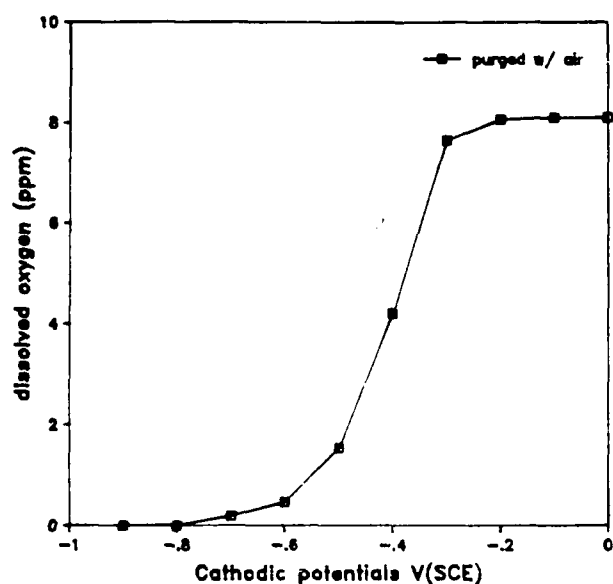
FIGURE 6. Metal surface DO as a function of applied cathodic potential in 3.5% artificial seawater purged with air
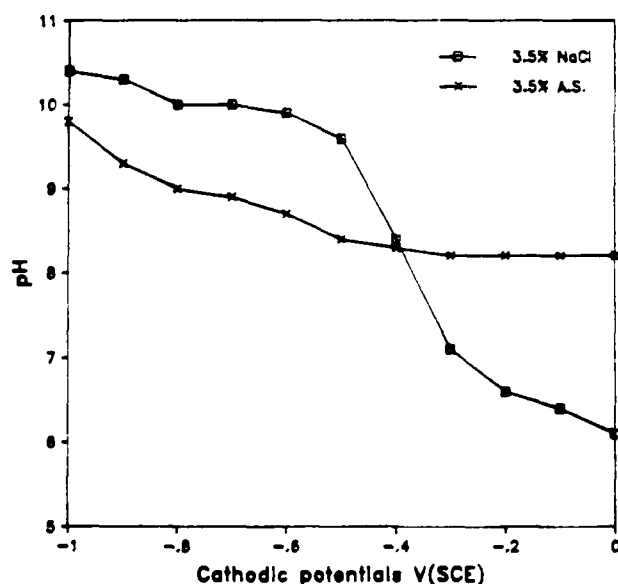

FIGURE 7. pH as a function of applied cathodic potential in 3.5% artificial seawater (AS) and 3.5% sodium chloride (NaCl), purged with air.

and the resulting cathodic polarization curve after treatment is essentially the same as at the beginning of the experiment.

The DO profiles in the agar layer reflect the microbial respiration activity during the experiment (Figures 9 and 10). The agar layer without microorganisms does not show any significant oxygen consumption after 14 h (Figure 9). The biotic agar layer exhibits significant oxygen consumption, which results in anaerobic conditions at the metal surface. After glutaraldehyde treatment, the DO profile is similar to the profile in the abiotic agar layer. A slight consumption of oxygen has been detected in agar layer after glutaraldehyde treatment, which suggests that a small number of microorganisms survived the treatment and were still respiring (Figure 10).
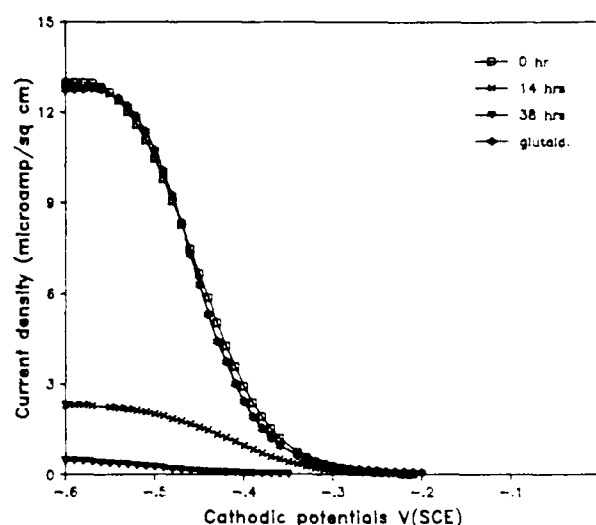

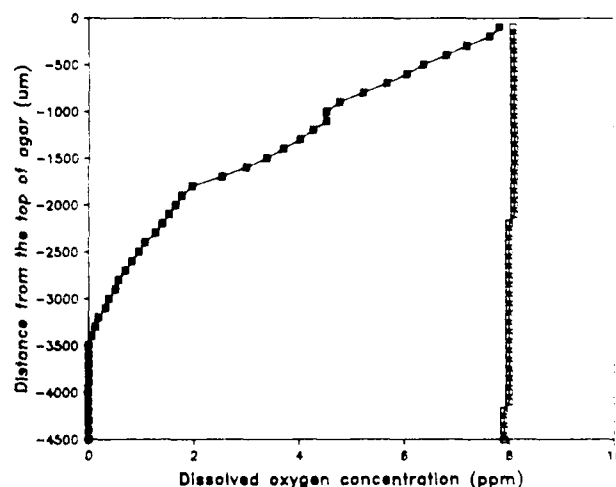FIGURE 8. The results of cathodic polarization measurements at corrosion coupons in an open channel flow reactor

FIGURE 9. DO profiles in agar films on corrosion coupons in the absence (□) and presence (■) of microorganisms after 14 h reactor operation.

DISCUSSION

Abiotic Experiment

Microelectrodes have been used to measure DO and pH at a cathodically polarized metal surfaces. The results can be analyzed based on chemical reactions that occur on cathodically polarized metal surfaces. Application of cathodic potential causes reduction of oxygen and release of hydroxyl ion according to reaction

$$1/2 O_2 + H_2O + 2e^- = 2OH^- \quad (1)$$
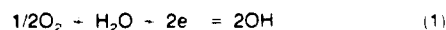
Reduction of oxygen occurs at the expense of increasing pH. Once the applied potential is more negative than the potential of the reversible hydrogen electrode, Reaction (1) is followed by
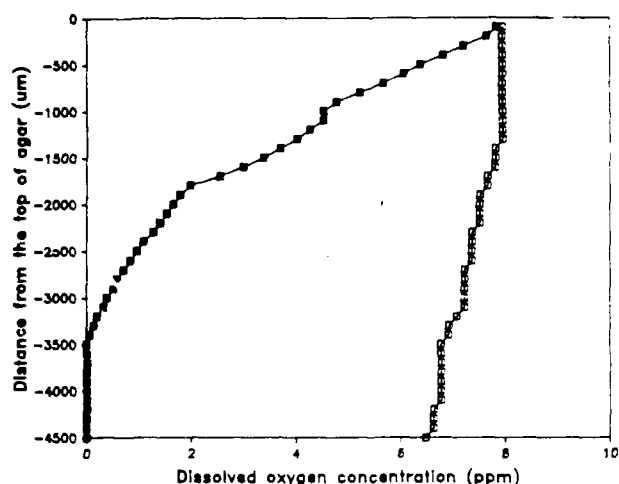
$$2H_2O + 2e^- = H_2 + 2OH^- \quad (2)$$
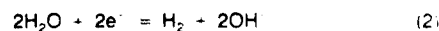
FIGURE 10. DO profiles in agar films or corrosion coupons in the presence of microorganisms before (■) and after (□) glutaraldehyde treatment.

which causes further increase in pH

The DO consumption curve (Figure 6) behaves accordingly Increasing the applied potential decreased the metal surface DO concentration. The asymptotic approach of DO to zero suggests that transport of oxygen from the bulk water may have been rate limiting. Otherwise, the curve would be linear. Oxygen diffusion rate from bulk to surface increases with DO at the metal surface decreases. Turbulence in the water phase caused by aeration in the PARC flask influences the DO flux into diffusion layer.

pH at the cathodically protected metal surface has been measured in two different systems, (1) sodium chloride and (2) artificial seawater. The metal surface pH varies with applied cathodic potential in different ways for the two solutions. Increasing applied potential increased the measured pH in both cases, which is consistent with theory [Equation (1)] and metal surface DO consumption (Figure 6). The shape of the pH curves (Figure 7), as a function of applied potential in the range zero to -0.8 V(SCE), reflects the changes in DO in the same range of applied potential (Figure 6). Further increase in potential below -0.8 V(SCE) causes release of hydroxyl ions [Equation (2)]. Results clearly indicate that the ionic constituents influence the pH obtained at a given DO concentration.

The flux of hydroxyl ions toward the bulk liquid from the metal surface during cathodic polarization is not the only factor that influences pH at the metal surface. An increase in cathodic potential causes oxygen reduction and release of hydroxyl ions. This is, in principal, similar to titrating the metal-water interface with strong base. The change in pH as a function of applied potential in sodium chloride is sigmoidal, while in artificial seawater, the change is minimal. For sodium chloride, the titration is for a strong acid with a strong base. In the case of artificial seawater, the carbonate buffering system acts as a weak acid

$$CO_2 + H_2O \rightarrow H_2CO_3 \qquad (3)$$

$$H_2CO_3 \rightarrow H^+ + HCO_3^- \qquad (4)$$

$$HCO_3^- \rightarrow H^+ + CO_3^{-2} \qquad (5)$$
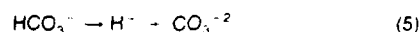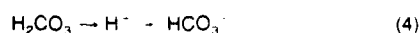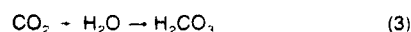
Hydroxyl ions, released as a result of cathodic polarization [Equations (1) and (2)] react with hydrogen ions [Equations (4) and (5)] and shift the reaction balance toward carbonate formation. The titration is for a weak acid with strong base. Thus, the bicar-

bonate in seawater is responsible for the shape of the pH vs applied potential curve

Theoretical calculations of pH at a cathodically polarized metal surface generally neglect the buffering capacity.[6] Theoretical surface pH calculations should include not only the flux of hydroxyl ions towards the bulk medium but also the flux of the buffering constituents from bulk toward the metal surface.

The influence of buffering capacity is very relevant for reactors used for microbial corrosion investigations. Experiments in the presence of microorganisms often last many days. If the products of electrochemical or microbial reactions are not removed from the system continuously, they can influence water buffering system considerably. This, in turn, influences the conditions at the metal surface. Continuous removal of reaction products is necessary for microbial corrosion investigations. Presence of microorganisms producing acid or hydroxyl ions as metabolic products at the metal surface does not necessarily cause changes in pH. Before considerable changes in pH can be observed the water buffering system has to be destroyed. It is possible to speculate that such a situation can exist inside a corrosion pit covered with biofilm. This situation, however, can also be created artificially by experimental conditions neglecting the proper replacement of water in a reactor Experiments conducted in closed reactors, which last many days especially in the presence of microorganisms, may result in dramatic changes in the water buffering system. This, in turn influences conditions at the metal-water interface and corrosion processes. Thus, open continuous flow reactors are desirable. One such reactor, an open channel flow reactor, was constructed for future investigations

Biotic Experiment

The open channel flow reactor proved its usefulness for microbial corrosion investigations. The reactor contained 24 circular coupons. Twelve of the coupons were covered with an artificial biofilm prepared by immobilizing microorganisms in a gel matrix Immobilization of microorganisms at the surface of corrosion coupons offers several advantages, including (1) microorganisms immobilized at the metal surface can be chosen according to experimental goals. (2) a 2% agar layer prevents bacterial contamination from the water, and (3) the agar layer prevents wash out of inoculum from the metal surface. Nutrient supply to the microorganisms and chemical inhibition are accomplished by transport through the agar layer. The relatively high number of coupons in the reactor allows replications and destructive sampling (e.g. cathodic polarization). A constant supply of nutrients and constant removal of products avoids the problems arising in a closed system because of changing water quality.

The results of cathodic polarization measurements in the presence and absence of microorganisms on the corrosion coupons confirmed expectations. Presence of microorganisms decreased measured current density resulting from consumption of oxygen by microorganisms thus decreasing its availability for cathodic processes (Figure 8). Direct measurements of the DO profile through the agar film confirmed this result. In the presence of microorganisms, DO was zero at the metal surface (Figure 9) Glutaraldehyde treatment was undertaken to prove that the observed phenomena was caused by the microorganisms presence After 14 h of glutaraldehyde treatment, the cathodic polarization curve was almost identical to that at the beginning of the experiment (Figure 8). The microorganisms were inactivated and oxygen was again available for cathodic processes. Measurements of the DO profiles in agar layer in the presence of microorganisms before and after glutaraldehyde treatment confirm this result The DO profile in the agar layer with immobilized microorganisms after glutaraldehyde treatment was similar to that in the agar layer without microorganisms present. A slight oxygen gradient suggests that some microorganisms survived the glutaraldehyde treatment and were still respiring (Figure 10)

Consumption of oxygen by microorganisms colonizing metal surfaces has implications for cathodic protection systems. If DO concentration at the metal surface is low, cathodic protection will not provide the expected increase in pH [Equation (1)]. From a practical standpoint, this means that the conditions at the metal surface may not be so conducive for calcareous deposition, as is expected from theory. This modifying effect can be magnified by high water buffering capacity. Decreases in buffering capacity make the metal-water interface sensitive to pH changes that may adversely influence the system from a corrosion standpoint when the metal surface is colonized with microorganisms. Microbial activity at the metal surface is generally "patchy," thereby resulting in nonuniform distribution of pH at the metal surface. The nonuniform pH, in turn, creates local action cells. High water buffering capacity protects against this mechanism. The higher the water buffering capacity, the more resistant the system is to changes in pH, which equalizes pH at the metal surface. This scenario is consistent with observations by Pisigan and Singley[10] that maximum corrosion rate is associated with minimum water buffering capacity. Stumm[11] also attributed increased corrosion rates to decrease in buffering capacity. The advantage of high buffering capacity is that the system is more resistant to changes in the metal surface pH caused by the presence of microorganisms. The disadvantage of high buffering capacity is that cathodic protection will not increase the metal surface pH and calcareous deposits may not form as expected.

The hypotheses are consistent with those in other literature. Dhar, et al.[12] investigated use of cathodic protection for decreasing the number of bacteria adsorbed on metals in seawater. The authors expected that bacteria would be adversely affected "because of in-situ electrochemical reduction of O_2 to H_2O_2 and OH^-." They observed that the decrease in bacterial numbers at an electrode immersed in sodium chloride, resulting from applying -0.3 (SCE) cathodic potential, was similar to applying -0.6 V(SCE) in seawater. In conclusion, they stated that the observed differences may have been caused by "the fact that the seawater has organic impurities that may be partly oxidized by H_2O_2, and also the possibility that, because of the considerable buffering capacity of seawater, the lethal effect of pH at the electrode would be minimal." The second hypothesis has been confirmed by results presented in this work.

CONCLUSIONS

▶ Direct DO and pH measurement at a metal surface immersed in water can be conducted with microelectrodes.

▶ pH at a cathodically protected metal surface is strongly influ-

enced by the buffering system of the electrolyte.

▶ Buffered electrolytes can reduce metal surface pH from theoretical expectations during cathodic polarization. Metal surface microbial activity has probably the same effect.

▶ Reactors for microbial corrosion investigations must provide for continuous removal of electrochemical and microbial reaction products. Accumulation of reaction products in the system may substantially influence water quality and change conditions at the metal surface, possibly causing artifactual results. Continuous supply of nutrients at relevant concentrations to the reactor is also preferred.

▶ An open channel flow reactor with microorganisms inoculated at the surface of corrosion coupons fulfills many of the requirements for microbial corrosion investigations.

REFERENCES

1. R. E. Tatnai, Mater Perf, Vol 20, No 8, p 32, 1981
2. S. Maxwell, Mater Perf, Vol 26, No 11, p 53, 1986
3. S. Elbek, A. C. C. Tseung, A. L. Mackay, Corros Sci, Vol 26, p 669, 1966
4. B. Little, P. Wagner, D. Duquette, "Microbiologically Induced Cathodic Depolarization," Paper No 370, CORROSION 87, NACE, Houston, Texas, 1987
5. L. C. Clark, R. Wolf, D. Granger, A. Taylor, J. Appl Phys, Vol 6, p 189, 1953
6. N. P. Revsbech, B. B. Jorgensen, Microelectrodes: Their use in Microbial Ecology, Advances in Microbial Ecology, Vol 9, K. C. Marshall, Ed., Plenum Publishing Corp, 1986
7. R. C. Thomas, Ion-Sensitive Intercellular Microelectrodes, Academic Press, p 49, 1978
8. G. K. Ackers, R. L. Steer, Biochem Biophys Acta, Vol 59, p 137, 1961
9. S. L. Wolfson, W. H. Hart, Corrosion, Vol 37, No 2, p 70, 1981
10. R. A. Pisigan Jr., J. E. Singley, J AWWA, Vol 79, p 62, 1987
11. W. Stumm, J San Eng Div, ASCE, Vol 86, p 27, 1960
12. H. P. Dhar, D. W. Howell, J. O. M. Bockris, J. Electrochem Soc, Vol 129, p 2178, 1982